MEASUREMENT AND SIGNIFICANCE OF THE WATER RETENTION PROPERTIES OF PAPERMAKING FIBRES

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Synopsis—Equilibrium water retention isotherms have been determined for papermaking fibres through the range of moisture contents that is of greatest papermaking interest.

The experimental method provides not only a measure of the swelling of the fibres and the equilibrium water retention at any force of water removal, but, conversely, the method measures the force with which the water is held and the force with which fibres or fibre elements are held together by residual water.

Factors affecting the mechanism of water retention and the amount of water held by fibres are demonstrated by the isotherms of model and papermaking fibres of widely varying properties and treatments. The part played by the mechanism and extent of water retention on the development of wet web properties during drying is discussed and the need is demonstrated for more information than is provided by the isotherm.

Finally, consideration is given to the role of swelling and water retention in pulp evaluation and some general principles are suggested by which the running and papermaking properties of a pulp might be predicted.

Introduction

THE purpose of this paper is to report an investigation of the cellulose/water relationship and of the relationship of the swelling and water retention properties of fibres to the basic process of papermaking. The work will be introduced by the discussion of a study that has had as its purpose the delineation of water retention isotherms of papermaking fibres over the range of moisture contents that are of the greatest papermaking interest. These measurements of equilibrium water retention will then be related to other methods for measuring the water associated with fibres and to their significance in papermaking.

Water retention isotherms

WATER retention isotherms have been obtained by an extension of a technique, originally applied to pulp fibres by Barkas,[1] which involves the measurement of the amount of water that is associated with a pad of pulp fibres when the water is subjected to a hydrostatic tension tending to remove it.

A water-saturated pad of fibres is placed on a saturated porous plate and the tension is applied either by exerting a suction below the plate as in the Barkas method or by applying a gas pressure above the plate as in the present method.

The pressure plate apparatus[2] is shown schematically in Fig. 1. The saturated pad and plate are mounted in a pressure vessel. The vessel is closed
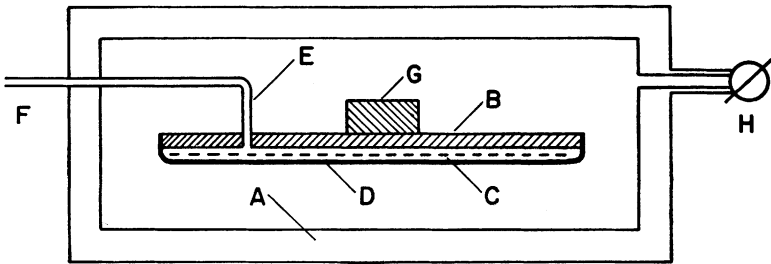

Fig. 1—Schematic diagram of the pressure plate apparatus: gas pressure, introduced at **H** into the pressure vessel **A**, forces water from the moist fibre pad **G**, through the wet porous plate **B**, through **E** to atmosphere at **F**; passage between the plate **B** and the rubber diaphragm **D** is maintained by a wire gauze **C**

and a controlled air or nitrogen pressure is applied. If the pores of the plate are sufficiently fine, water cannot be forced from the plate, but water is forced from the pad through the plate to atmospheric pressure at the outlet. This process continues until at equilibrium the hydrostatic tension, radii of curvature of the water menisci and the reduced vapour pressure above the curved water surfaces are everywhere the same. After this equilibrium is attained, the pressure is released, the pad is removed and its moisture content is measured. An isotherm is constructed after repetition of the determination at other pressures.

The relationship of the variables is given by the Kelvin equation[3]—

$$\ln (p/p_0) = -2\gamma M/rdRT \quad . \qquad . \qquad . \qquad . \quad (1)$$

where p = the equilibrium vapour pressure above a curved water surface,

r = the radius of curvature of the water surface,

p_0 = the equilibrium vapour pressure above a plane water surface,

d = the density of water,

γ = the surface tension of water,

R = the gas constant,

M = the molecular weight of water,

T = the absolute temperature

and by an equation relating the applied pressure or the hydrostatic tension P with the surface tension and the radius of curvature r—

$$P = -2\gamma/r \quad . \quad . \quad . \quad . \quad . \quad (2)$$

With these two equations, it is possible to make the calculations required to compile Table 1.

TABLE 1—CALCULATIONS BASED ON THE KELVIN EQUATION: TEMPERATURE 25° C

Relative vapour pressure	1—RVP	P, dyn/cm²	r, cm
0.999990	10^{-5}	1.36×10^4	1.06×10^{-2}
0.99990	10^{-4}	1.36×10^5	1.06×10^{-3}
0.9990	10^{-3}	1.37×10^6	1.05×10^{-4}
0.990	10^{-2}	1.38×10^7	1.04×10^{-5}
0.98	2×10^{-2}	2.77×10^7	5.19×10^{-6}
0.95	5×10^{-2}	7.04×10^7	2.04×10^{-6}
0.90	10^{-1}	1.45×10^8	1.00×10^{-6}
0.80	0.20	3.06×10^8	4.70×10^{-7}
0.70	0.30	4.90×10^8	2.94×10^{-7}
0.60	0.40	7.01×10^8	2.05×10^{-7}
0.50	0.50	9.51×10^8	1.51×10^{-7}

1 psi = 6.89 + 10⁴ dyn/cm²   1 atm = 1.013×10^6 dyn/cm²   1 cm Hg = 1.333×10^4 dyn/cm²

The mechanism by which equilibrium is reached cannot yet be discussed quantitatively. At low tensions and high moisture contents, equilibrium is attained primarily by capillary conductivity—that is, by flow of liquid water from the pad to the plate or from regions of low to high meniscus curvature.[4] As moisture contents decrease, however, the capillary movement becomes very slow and it is assumed that evaporation-condensation processes contribute increasingly to the attainment of equilibrium.

A typical isotherm is plotted in Fig. 2 as a function of pressure or equivalently as a function of (1—relative vapour pressure). The pulp is a never-dried, unbeaten, unbleached sulphite. It is to be noted that the amounts of water retained by the fibres decrease from just over 3 cm³ water/g fibre to about 0.75 cm³/g—that is, from 25 per cent dry to 57 per cent dry. This represents a range that is of interest in the study of the consolidation of the paper web between the couch and the middle of the dryers.
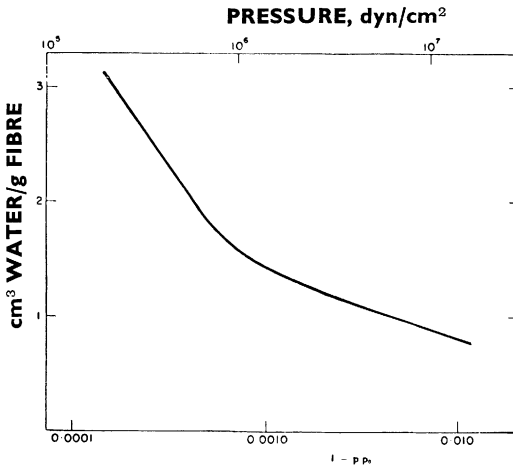
PRESSURE, dyn/cm²

Fig. 2—Typical water retention curve for
undried unbeaten spruce sulphite pulp

Water is retained by papermaking fibres by several possible mechanisms. The total associated water includes (a) water held to the internal and external surfaces by hydrogen bonding, (b) water held in the capillaries or pores that result from the microfibrillar structure of the cell wall, (c) water occluded in the lumen of the fibre, (d) capillary water held on the surface of the fibre by fibrillation and (e) water associated with hydrophilic material sorbed in or on the fibres. It is assumed that the isotherm primarily measures the reduction in the amount of capillary water, internal or external, as increasing forces of water removal are applied.
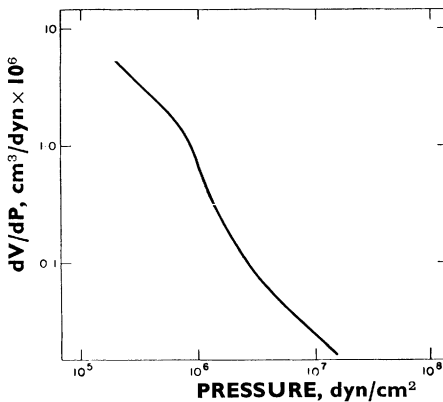

PRESSURE, dyn/cm²

Fig. 3—Differential plot of Fig. 2 (logarithmic)

The lowest pressure shown is 0.2 atm $(2 \times 10^5 \text{ dyn/cm}^2)$. Although the isotherm can be carried to lower pressures, it will be seen from work to be described later (Fig. 13) that the retained water then includes a substantial proportion of interfibre capillary water. Since this water is a function of pad structure rather than of the retention properties of the individual fibres, an initial pressure has been selected arbitrarily such that, for most papermaking fibres of interest, free interfibre capillary water will be absent.
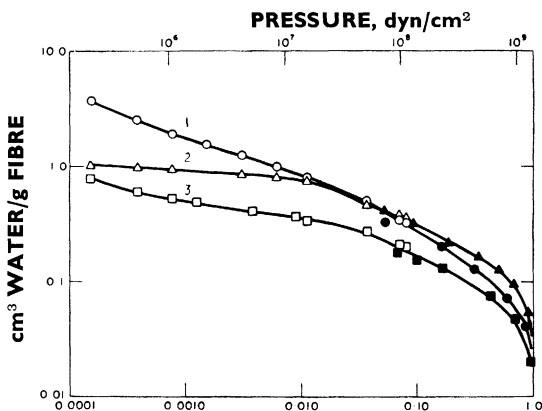

Fig. 4—Comparison of pressure plate and membrane data (open points) with desorption isotherms obtained from the literature (solid points)—(*1*) sulphite pulp,[6] (*2*) viscose rayon,[7] (*3*) cotton[8]

The change of slope of the isotherm in Fig. 2 and in the differential curve in Fig. 3 suggest a possible change in mechanism of water retention at pressures between 0.6 and 1.5 atm $(0.6-1.5 \times 10^6 \text{ dyn/cm}^2)$, when the equivalent radii of curvature are 1.0–2.4 μ—equation (*2*). The rapidly decreasing slope may be related to the transfer of water retention mechanism from the level of fibre dimensions (as in emptying or collapse of the lumen) to capillary spaces of smaller dimensions.

The highest pressure is dictated by the porosity of the plate. With the present plate, pressures in excess of 15 atm cause gas to bubble through the plate and permit evaporative drying of the samples. Finer plates or permeable membranes are available that permit the use of higher pressures and these have been used in specific instances to extend the isotherms (see Fig. 4).

The water retention at 15 atm $(1.5 \times 10^7 \text{ dyn/cm}^2)$ corresponds to a relative vapour pressure just below 0.99, and conditions are thus approaching those that may be attained by the classical method of desorption into a controlled

environment using a desorption balance or a vacuum desiccator. The data obtained with these latter methods at relative vapour pressures much greater than 0.95 are considered, however, to be uncertain because of experimental difficulties primarily related to temperature control and the time required to reach equilibrium.[5]

An attempt to consolidate data from the pressure plate and desorption methods into a single isotherm appears in Fig. 4 for three diverse fibres. The desorption data are taken from the literature[6-8] and pertain to similar, but not identical fibre samples. The correspondence is reasonably good despite the difference in the origin and treatment of samples and the differences in the conditions of desorption.

TABLE 2—WOOD DENSITY AND WATER RETENTION

Species	Density, g/cm³	Lumen diameter/ fibre diameter	Isotherm Fig. 6	Collapsibility index*
E. grandis	0.406	0.619	1	0.98
E. saligna	0.580	0.518	2	0.44
E. resinifera	0.708	0.217	3	0.14
E. propinqua	0.765	0.214	4	0.22

* Discussed later in this paper and in another paper ([9])

It is observed that the curvature of the isotherm appears to be continuous and this suggests that any fibre saturation point must depend on some arbitrary definition, if it is to be based on desorption isotherm data.

Thus, the equilibrium water retention isotherm may be extended by using data obtained by classical desorption methods. This isotherm represents the relationship between the moisture content of the fibres and the relative vapour pressure or relative humidity with which they are in equilibrium. So long as equations (*1*) and (*2*) are valid, the relative vapour pressure can be related to the force required to remove further water. Alternatively, the force may be regarded as a tension in the residual water, tending to draw and hold the fibres or elements of fibres together.

Model fibres

WATER retention isotherms have been determined for several model fibres and are illustrative of some of the principles involved. The isotherms in Fig. 5 correspond to—

1. Glass fibres, chopped, 0.5μ nominal diameter: non-porous. Interfibre capillarity due to the very fine fibres.

2. High yield sulphate pulp: rigid fibre with large non-collapsing lumen.

3. Hollow filament rayon:[9] fine pores, large easily collapsed lumen.

4. Fibrillated viscose rayon:[10] fine pores, external fibrillation.
5. Viscose rayon (not fibrillated): fine pores, little external capillarity (30 μ nominal diameter).

Isotherms for the first four samples show steep downward slopes at the lower applied pressures, then level off at a low retention value. This level part of the isotherm indicates a structure in which few capillaries of the
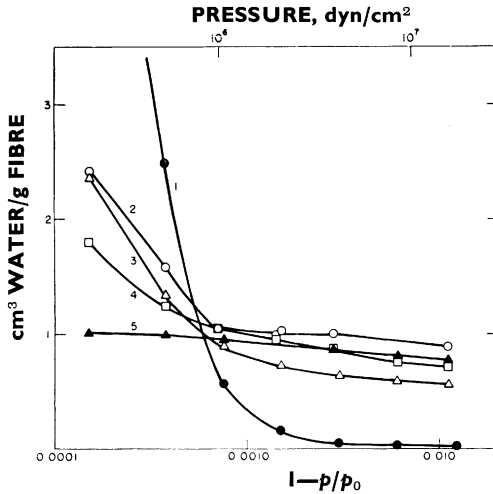

Fig. 5—Water retention isotherms for model fibres—(*1*) glass, 0.5 μ, (*2*) high yield spruce sulphate, (*3*) hollow filament rayon, (*4*) fibrillated rayon, (*5*) textile viscose

critical size (Table 1) are present. The initial falls are primarily due to the respective separate effects of (*1*) loss of interfibre water, (*2*) emptying of a rigid lumen, (*3*) collapsing the lumen and (*4*) decrease in water held by external fibrillation. The flat isotherm corresponding to (*5*) indicates relatively compact incompressible fibres without pores or voids of the sizes that would be emptied within the range of applied tensions.

Papermaking fibres

IF these model isotherms are compared with Fig. 2, it is seen that the isotherm for the papermaking fibre shows a relatively steep decrease throughout the whole range, indicating either a wide distribution in the size of water retention elements or the superposition of several or all of the proposed retention mechanisms.

TABLE 3—HEMICELLULOSES AND WATER RETENTION

Sample	*Pentosan, per cent*	*Isotherms (Fig. 11)*	
		Undried	*Dried*
Untreated holocellulose	22.5	1	4
Holocellulose treated with sodium hydroxide for 1 h at—			
1 per cent	20.8	—	—
3 per cent	17.0	2	5
6 per cent	6.7	2	—
10 per cent	6.4	3	6

The water retention properties of papermaking fibres are believed to be affected by both macro- and micro-structure and to depend on lumen size, collapsibility, porosity and pore size distribution and external fibrillation. It should be emphasised that the decrease in water retention as the applied pressure is increased is due both to emptying of rigid capillaries and the progressive collapse of deformable capillaries. Since the relative importance of the two processes is not known, only the most general conclusions can be drawn from the isotherms about the pore sizes, pore size distributions or areas of pores.
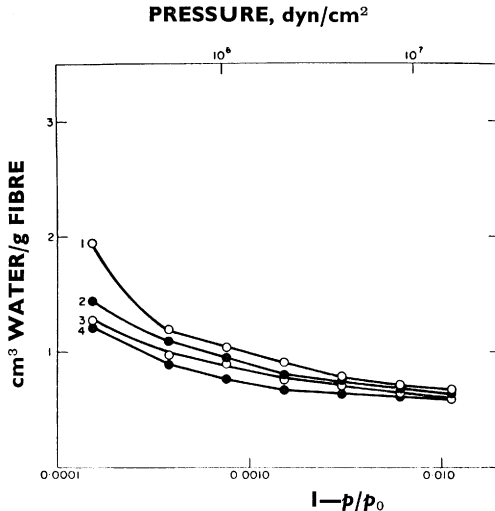

PRESSURE, dyn/cm²

cm³ WATER/g FIBRE

$1—p/p_0$

Fig. 6—Water retention isotherms for kraft eucalyptus pulp of various species—(*1*) *E. grandis* (*2*) *E. saligna* (*3*) *E. resinifera* (*4*) *E. propinqua* (see Table 2)

The isotherms obtained with woodpulps thus depend on a number of variables, some of which are illustrated in Fig. 6–11—

(*a*) An effect of morphology is observed in Fig. 6, in which the isotherms for eucalypt kraft pulps of four different species (Table 2) are compared. The isotherms, which tend to converge at the higher applied pressures, are separate at the lower end and show increasing water retention per unit weight of fibre as the wood density is lower and the lumen volume higher. Convergence presumably
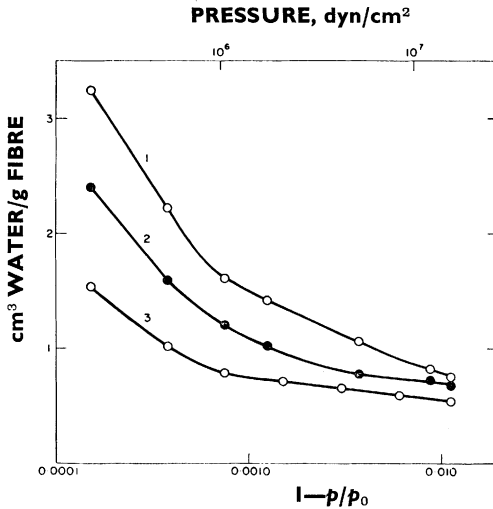
PRESSURE, dyn/cm²

Fig. 7—Water retention isotherms for un-
beaten spruce sulphite—(*1*) never-dried, (*2*)
air-dried, (*3*) air-dried, held at 105°C, 95 per
cent rh for 16 h

results from the collapse or emptying of the lumen and the larger pores in the less dense wood and suggests that the fine structure may be similar in the four samples.

(*b*) The effect of drying and drying conditions is demonstrated in Fig. 7. A drying/rewetting cycle reduces the water retention properties throughout the range and an increase in the severity of the drying treatment produces greater losses of water retention properties. The decrease in water retention after pro-longed drying is believed to be due to a relaxation, during the drying treatment, of the internal stresses that promote swelling when the fibres are reimmersed. The relaxation of the stresses is greater as the time, temperature or relative humidity of the treatment of dried or collapsed fibres is greater.[11]

(*c*) Fig. 8 shows the isotherms for a dry lap, commercial unbleached kraft pulp, unbeaten and beaten to 400 csf. Isotherms are shown also for individual classifier fractions of the beaten pulp. The large differences in retention properties

that are evident at low applied pressures tend to disappear at the higher pressures, as the phenomena are transferred from larger capillary dimensions to smaller ones. Beating thus appears to create capillary effects confined mainly to the low pressure end of the isotherm. This observation appears to substantiate earlier observations that the moisture regains of beaten and unbeaten pulps are similar
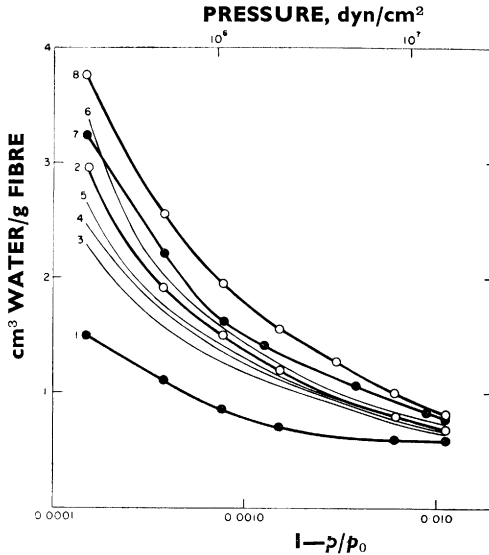

Fig. 8—Water retention isotherms for beaten and unbeaten pulps—(*1*) unbeaten dried standard sulphate, (*2*) sulphate beaten 400 CSF, whole pulp, (*3*) ditto classified, R14, (*4*) ditto, 14/28, (*5*) ditto, 28/48, (*6*) ditto, 48/200, (*7*) never-dried spruce sulphite unbeaten, (*8*) sulphite beaten 400 CSF

when determined by classical sorption or desorption methods.[6] The convergence is apparent also with never-dried pulps—beaten and unbeaten—and the isotherms become identical at the highest applied pressure.

(*d*) Modification of the cellulose structure can play a considerable role also in the water retention properties. In Fig. 9, pulps that have been cross-linked with formaldehyde[12] in the swollen condition and in the dry state are compared with untreated pulps, before and after drying.

The isotherms indicate that, when fibres are cross-linked in the swollen condition, a drying/rewetting cycle results in little change in water retention, whereas an untreated pulp shows appreciable irreversible collapse. A dried fibre, cross-linked in the nearly dry state takes up and holds only half the water that is taken

up by an untreated fibre. Any unqualified generalisation that one is tempted to make about swollen volume and paper strength is contradicted by the wet cross-linked fibres (Fig. 9, isotherms 3 and 4), which have very poor papermaking properties.

(*e*) The isotherms for cotton linters, alkali linters[13] and hydroxyethylated linters[14] are compared in Fig. 10. The increased hydrophilic properties of the treated samples are evident in the general level of the isotherms.
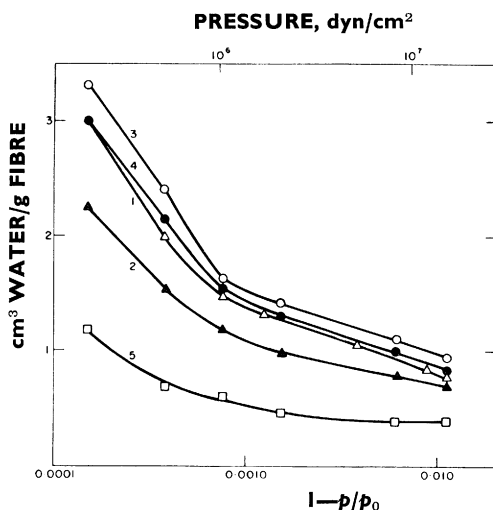

Fig. 9—Water retention isotherms for cross-linked fibres—(*1*) spruce sulphate untreated, never-dried, (*2*) sulphate, air-dried, (*3*) sulphate cross-linked when wet, never-dried, (*4*) sulphate cross-linked when wet, air-dried, (*5*) sulphate cross-linked when dry

(*f*) Hemicellulose is a hydrophilic component of papermaking pulps and should contribute to the isotherms. The effect of varying the hemicellulose content of a delignified high yield birch kraft pulp is shown in Fig. 11 for both undried and dried samples. The pulp characteristics are in Table 3.

Contrary to expectations, the stepwise decrease from 22.5 per cent to 6.7 per cent pentosan (by treatment with 1, 3, or 6 per cent sodium hydroxide) produced no significant changes in the isotherm. The treatment with 10 per cent caustic, however, changes the character of the isotherm, but the isotherm is lowered only at the low pressure end. A decrease in water retention is in line with the results of others.[15] The observation that only the initial part of
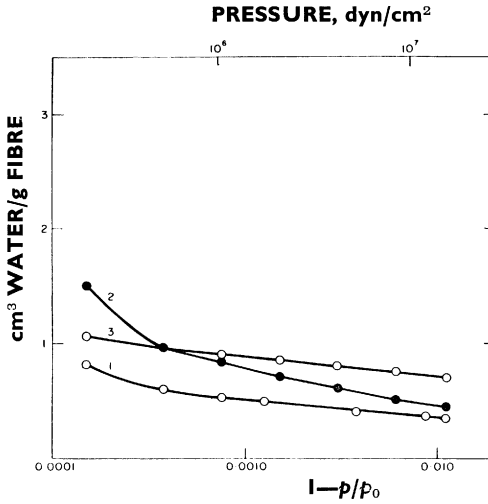
PRESSURE, dyn/cm^2

Fig. 10—Water retention isotherms for cotton linters—(*1*) untreated, (*2*) hydroxyethylated, (*3*) alkali linters
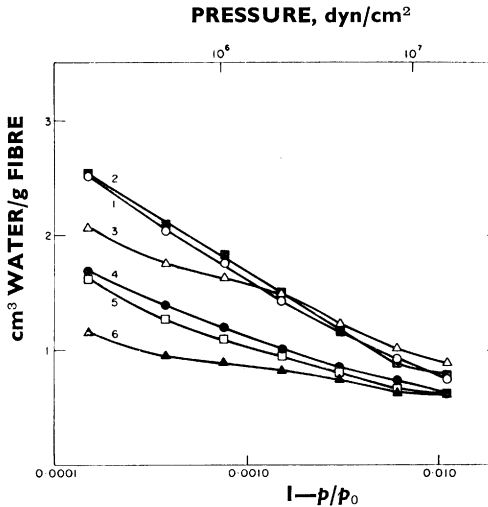
PRESSURE, dyn/cm^2

Fig. 11—Water retention isotherms at different hemicellulose contents—(*1*) birch holocellulose, (*2*) after 3 per cent or 6 per cent alkali, (*3*) after 10 per cent alkali, (*4*) holocellulose, air-dried, (*5*) 3 per cent sample, air-dried, (*6*) 10 per cent sample, air-dried

8—C.P.W. I

the isotherm is involved and that the difference in hemicellulose content between the 6 per cent and 10 per cent caustic extraction is small suggests that the significant change is the effect of caustic treatment on the morphology of the fibre rather than on its hemicellulose content. It may be that a distortion or collapse of the fibre occurs when the caustic is replaced by water.[16]

After a drying/rewetting cycle, the greater recovery of the hemicellulose-rich pulps is to be expected.

The foregoing examples indicate that the water retention properties of papermaking pulps can vary over a wide range and that fibre morphology, drying history, beating, chemical modification, caustic treatment and other factors have their effect on the isotherms.

Because water retention can be affected by so many variables, the isotherm of an unknown sample can give only limited information about the fibres. It measures the amount of water retained at given forces of water removal, but the mechanisms of water retention involved cannot be specified and the porosity characteristics, fibrillation, collapsibility, hemicellulose swelling and so on must be determined by other means. There is some evidence that, from the point of view of papermaking, the gross water retention properties are less important than the mechanisms by which the water is held.

Mobility of retained water

ALTHOUGH the equilibrium water retention properties of fibres are of considerable interest in papermaking, a comparable importance attaches to the mobility of the retained water and its ease of removal. A few experiments have been designed to illustrate how this mobility varies with retention.

The pressure plate technique was modified to provide a method for measuring the rate of water removal from the pad. A pad of standard weight is allowed to come to equilibrium at some selected pressure with the implication that the moisture distribution has become uniform throughout the pad. The pressure is then increased and the volume of water expressed from the pad is measured from time to time. The rate of water removal is plotted as a function of time in such a way that an extrapolation provides an indication of the initial rate of water removal. This rate divided by the applied pressure is a measure of the mobility of the water at the initial equilibrium moisture content. Data obtained in this way are plotted in Fig. 12.

Fig. 12 also includes mobility data obtained by a method, similar to that of Parker,[17] which is used to measure the permeability of unsaturated (air-intruded) pads of pulp fibres at definite moisture contents. The permeability falls very rapidly with initial air intrusion, then less strongly. This curve has been arbitrarily matched with the pressure plate outflow data to give com-

posite curves. Each method involves simplifying assumptions that preclude the calculation of a rigorously defined flow resistance or capillary conductivity,[18] but the general shape of the curve and the comparison of a never-dried pulp with a dried, stored pulp are significant and demonstrate how greatly the water mobilities can differ for two unbeaten pulps at the same moisture content.

cm³ **WATER/g FIBRE**
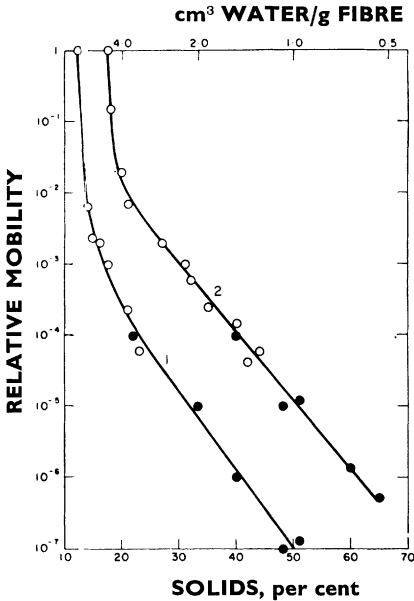
Solid points give pressure plate drainage data; open points give permeability data—(*1*) spruce sulphite never-dried, (*2*) spruce sulphite, dried, long storage

The mobility is measured relative to the mobility of water in a saturated pad and is based on the volume of flow from a unit cross-section of a standard pad under unit hydrostatic tension

Fig. 12—The relative mobility of retained water at various pad moisture contents

SOLIDS, per cent

Hydrodynamic specific volume and dye migration measurements

IF the pressure plate experiments are extended by applying pressures or tensions less than 0.2×10^6 dyn/cm², one may obtain isotherms as shown by the experimental points in Fig. 13.

The pads remain saturated at the lowest pressures and contract without air intrusion to the points *A*, beyond which interfibre water is removed and is replaced by air. Beyond *B* (0.2×10^6 dyn/cm²), the isotherms are similar to those already reported. The low pressure isotherms depend rather strongly on the formation, structure and mechanical properties of the pad rather than on the water retention properties of the fibres themselves. It has been assumed that the isotherms between *A* and *B* represent the removal of interfibre capillary water and 0.2×10^6 dyn/cm² has been arbitrarily selected as the initial point on the isotherms that have been reported in Fig. 5–11.

Although only a few low pressure isotherms have been investigated in this work for the reasons outlined, they could be of considerable interest in relation to the mechanical properties of fibre aggregates. Barkas used porous plate techniques to investigate the bulk modulus of fibre structures and to attempt the determination of the elastic properties of fibre pads.[19] The isotherms in conjunction with simultaneous pad volume measurements can provide considerable information concerning pad compressibility, air intrusion phenomena and interfibre capillarity.[20, 21]
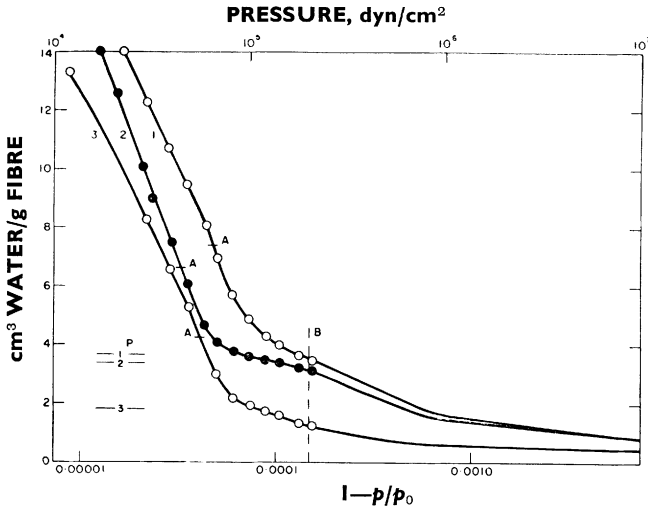

Fig. 13—Water retention isotherms extended to lower pressures—(*1*) never-dried spruce sulphite, (*2*) high-yield sulphite, (*3*) dried, stored sulphite

Points A indicate region of first air intrusion; retention levels P indicate water associated with fibres as measured by the permeability method; the usual isotherms are plotted beyond B

The levels of water retention indicated by *P* in Fig. 13 are calculated from the hydrodynamic specific volume of the fibres. This specific volume is measured with fibres in suspension or in a saturated pad, thus in the absence of surface tension forces. The measurement is made either by the permeability method[22] or by the measurement of the specific filtration resistance.[23, 24] The two methods give comparable results,[25] if the rates of flow or filtration are kept low enough that the fibres are not deformed by fluid drag.[26] It has been assumed[20, 21] that the hydrodynamic specific volume of the fibres

includes all the water associated with the fibres by all mechanisms and this amount can be therefore calculated from permeability data. This value may be considered to be an equilibrium water retention value at zero force of water removal.

The amount of associated water calculated from the specific volume is always greater than the water retention measured on the porous plate at 0.2 atm by an amount that is related to the distortion of the fibre, the collapsibility of the surface fibrillation or the collapsibility of the fibre itself.

Some values of associated water as measured by the permeability method and the porous plate method at 0.2 atm are given in Table 4 to illustrate the range of values. Both of these measurements of 'swelling' have previously[11, 20, 21, 27] been used to compare pulps or to follow the changes resulting from beating, drying or other treatments. As such, they are useful indices of change in the structure or mechanical properties of fibres and correlations between them and paper strength have been pointed out.[11, 27, 28]

TABLE 4—MEASUREMENTS OF WATER RETENTION
(in cm³ water/g fibre)

Fibre and treatment	*Permeability specific volume*	*Retention at P = 0.2 atm*	*Dye migration end point*	*Collapsibility index*
Sulphite, unbeaten, undried	3.76	3.24	1.32	1.92
Sulphite, beaten 400 CSF	4.55	3.76	1.38	2.38
Kraft, dry lap	2.34	1.50	0.89	0.61
Kraft, dry beaten	3.65	2.96	0.89	2.07
Kraft, high yield	2.29	2.18	1.86	0.32
Sulphite, high alpha	1.40	1.12	0.58	0.54
Viscose rayon	1.09	1.00	1.01	0.0
Fibrillated rayon	2.00	1.80	0.85	0.95
Hollow filament rayon	3.16	2.11	0.70	1.41

A further test that we have found useful is the dye migration test, which depends upon the mobility of the retained water. This method—described elsewhere[20, 29]—measures the moisture content at which the migration of liquid water from fibre to fibre under the action of capillary forces becomes negligible. The end point is in practice fairly sharp and a critical moisture content can be determined that is usually reproducible to ± 0.03 cm³ water/g fibre. It differs from the previous measurements in that it is not an equilibrium method, although the results are largely independent of test conditions. It depends not only on the water retention properties of the fibre, but upon the mobility of the retained water. The end point has been interpreted[21] as the point in the drying process at which all extra-fibre water is removed from the

web and the surface of the fibres becomes 'dry'. The method thus arbitrarily differentiates mobile and immobile water. As will be seen, the end point is related to the onset of bonding and fibre shrinkage.

The difference between an equilibrium water retention value—such as that based on the permeability specific volume or a pressure plate retention value at some specified pressure (say, 0.2 atm)—and the water content at the dye migration end point appears to measure in a significant way the collapsibility of the fibres. The collapsibility index thereby obtained (Tables 2 and 4) has shown a reasonable correlation with fibre flexibility or deformability,[9, 21] which in turn has been correlated with fibre flocculation in suspensions[30] and with wet web strength.[30, 31]

The experimental methods based on permeability, on pressure plate techniques and on dye migration provide complementary measurements of the cellulose/water relationship. It is now of interest to see how far these measurements are significant in papermaking. Inasmuch as the measurements are obtained under static or quasistatic conditions and the processes on the papermachine characteristically involve non-equilibrium phenomena occurring in response to transient forces, it is not to be expected that quantitative predictions can be made from pulp evaluation to papermachine operation—nor have these yet been attempted.

It has been possible, however, to establish some relationships between the water retention values discussed and the basic papermaking process as carried out in the laboratory on handsheets.

Wet web properties

WHEN a web is formed by draining a suspension of papermaking fibres and the web is progressively dried by slow evaporation of the water, there are several changes in web properties that can be related to various stages of water removal. These points can be recognised most readily in a plot of wet web strength as a function of moisture content, although equivalent behaviour can be noted by following the caliper, opacity, electrical conductivity, we web tear or stretch.[20, 21]

The process divides itself (Fig. 14) readily into—

AB. Web consolidation without air intrusion.
 B. Air intrusion, followed by
BC. Removal of interfibre capillary water.
 C. First strength inflexion when removal of free interfibre capillary water is complete.
CD. Removal of water associated with fibrillation and lumen.
 D. Second strength inflexion.
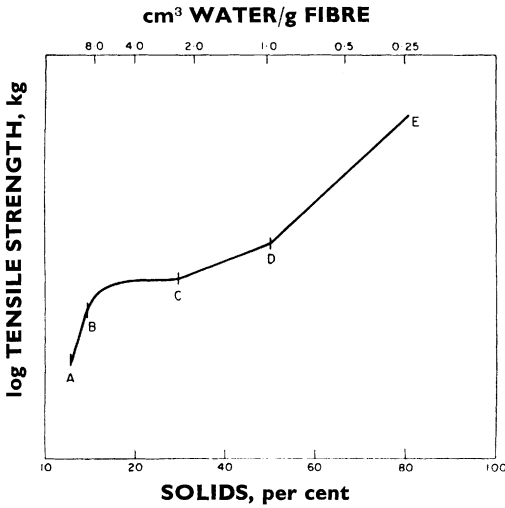**DE.** Onset and development of interfibre bonding.

cm³ WATER/g FIBRE

8·0 4·0 2·0 1·0 0·5 0·25

log TENSILE STRENGTH, kg

E

D

C

B

A

10 20 40 60 80 100

SOLIDS, per cent

Fig. 14—Schematic curve showing the development of sheet strength as the wet web is progressively dried—**A**, at formation, **B**, at air intrusion, **C**, first strength inflexion, **D**, second strength inflexion

cm³ WATER/g FIBRE (PERMEABILITY)

5

4

3

2

1

0
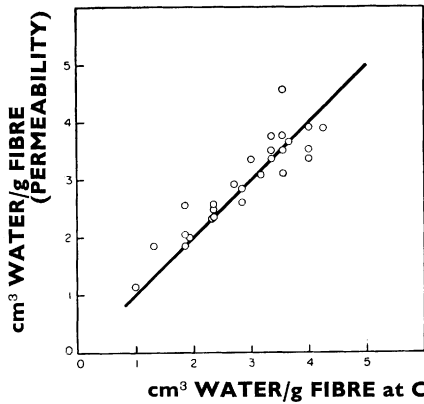
0 1 2 3 4 5

cm³ WATER/g FIBRE at C

Fig. 15—Correlation of the abscissae of point C (Fig. 14) with the amounts of associated water calculated from the hydrodynamic specific volume (permeability) for a variety of woodpulps and other cellulose fibres

In a typical unbeaten, never-dried, softwood chemical pulp the significant points B, C and D may be respectively at 14, 25 and 45 per cent solids or at 6.1, 3.0 and 1.2 cm^3 water/g fibre. The first of these (B) is determined to a large extent by the geometry of the web, by the flexibility and morphology of the fibres and by interfibre friction, whereas the remaining two (C and D) are functions of the water retention properties of the fibres.

The correlation of C with the permeability specific volume (Fig. 15) has been commented on previously[20, 21] and has been further substantiated by additional experimental work. The first strength inflection corresponds to the removal of the last of the free interfibre capillary water or the first of the associated water.

The reality of D as a critical region in the drying of wet webs is attested to by the variety of phenomena that are observed to occur at or near this value—

1. The wet web strength begins to increase strongly (Fig. 14 and Fig. 16, curve 1).
2. The strength of wet webs measured after immersion in a water-miscible liquid begin to show appreciable strength (Fig. 16, curve 2). The demonstration is of fibre interactions in the absence of surface tension forces.
3. The force required to peel apart two webs that have been dried in contact increases sharply (Fig. 16, curve 3). This experiment is designed to measure interfibre adhesion in the absence of fibre entanglement.
4. Planar shrinkage becomes evident in webs of unbeaten fibres as measured by tension development at constant length (Fig. 16, curve 4) or length decrease at constant tension.
5. A decrease in the effect of surface tension reduction is demonstrated in an experiment in which a surfactant is added to drying webs at different points in the drying process and the dry paper strength is measured (Fig. 16, curve 5).
6. The effectiveness of wet pressing on the strength of the dry paper falls off rapidly as the pressing is carried out at higher and higher solids contents (Fig. 16, curve 6).

This accumulation of experimental evidence indicates that moisture contents in the vicinity of 1.1–1.3 cm^3/g (43–48 per cent solids) are significant for never-dried chemical pulps, because they involve a change in the magnitude of interfibre forces and probably a change in the mechanism of sheet coherence. The same phenomena occur at a lower moisture content (0.55–0.8 cm^3/g) for the fibres that have been through a drying/rewetting cycle.[11]

This critical range of moisture contents lies within the range of the water retention isotherms that we have determined. If the applied pressure is plotted as a function of solids content (Fig. 17, curve 1), the similarity to Fig. 16, curves 1, 3 and 4, is apparent. The change in properties (strength,

shrinkage, peeling resistance, etc.) can therefore be related to an increase in tension in the decreasing residual water.

It is not possible, however, to ascribe all the property changes in the drying
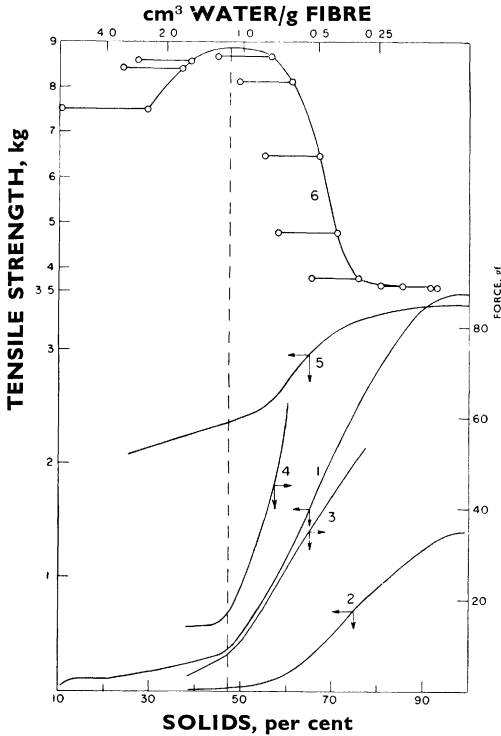

Fig. 16—Development of various properties during the drying of a wet web (never-dried spruce sulphite pulp)—(*1*) tensile strength, (*2*) tensile strength, immersed in dioxane, (*3*) intersheet adhesion, peeling, (*4*) shrinkage stress development, (*5*) paper strength after surface tension reduction in the wet web at various solids contents, (*6*) paper strength as a function of the solids content at which the web was wet pressed; the changes in solids content during pressing are shown by the horizontal lines

wet webs to the existence of surface tension effects at the time of testing. The testing of wet webs immersed in dioxane (Fig. 16, curve 2) or other non-swelling, water-miscible liquid shows a development of strength that must be

attributed to an interfibre cohesion or friction, which begins to develop in the critical moisture region (D) and which persists in the absence of a gas/liquid interface. The effects of reducing surface tension at various stages of wet web drying (Fig. 16, curve 5) give further evidence of the development of a more permanent type of interfibre bonding.
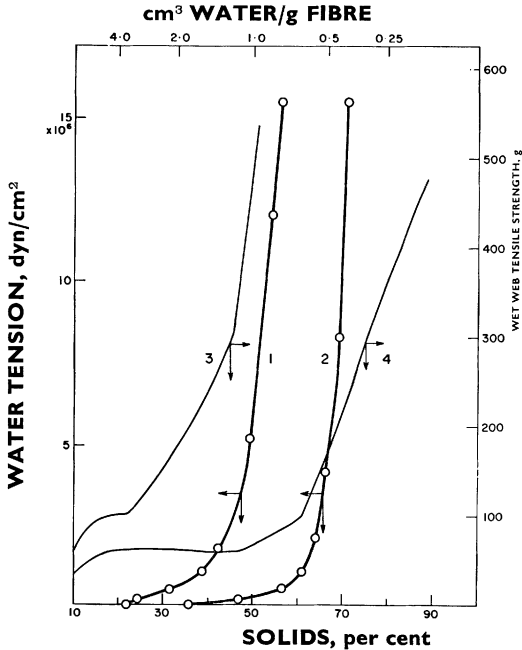

Fig. 17—Hydrostatic tension in the residual water at various solids contents—(*1*) unbleached unbeaten undried sulphite pulp, (*2*) dried, stored sulphite; the corresponding wet web tensile curves are shown— (*3*) undried pulp, (*4*) dried pulp

Whether or not the strength increases near 50 per cent solids are due to the development of cellulose–cellulose hydrogen bonds, it is apparent that the tension developed in the decreasing residual water has brought the fibres into intimate contact to the extent that the web coheres in the absence of an air/ liquid interface.

Examination of a number of isotherms fails to suggest any way to predict a critical moisture content that might be used to establish a quantitative correlation between equilibrium water retention properties and the web

properties—strength, shrinkage, etc. Although no well-defined singularity appears in the isotherm, it may be of some significance that, for fibre samples corresponding to Fig. 2, the shrinkage and strength development become evident at tensions (4–6×10^6 dyn/cm^2), which correspond to the straightening of the differential curve (Fig. 3) and presumably to the end of water removal processes at the fibre level and to the completed transfer of processes to the submicron level.
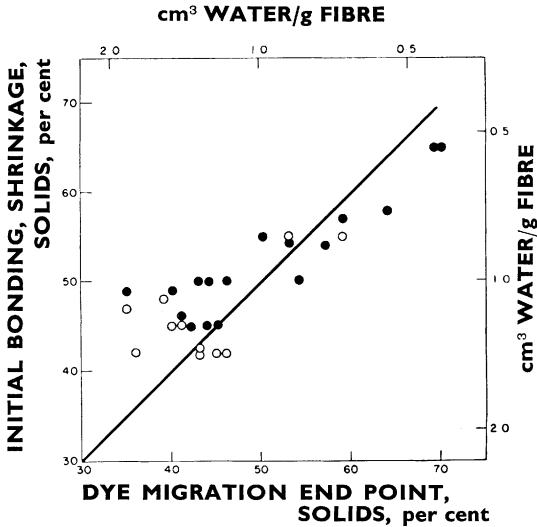

Fig. 18—Correlation of the dye migration end point with phenomena occurring at D (Fig. 14) using unbeaten pulps—closed circles represent inception of shrinkage stress during drying, open circles represent initial intersheet adhesion

In earlier work,[21] a correlation was demonstrated between the dye migration end point and the various phenomena occurring near D (Fig. 14 and 16). This permitted the prediction of the point of shrinkage or interply adhesion (Fig. 18) for a wide variety of fibres, although reservations had to be made in applying the test to fibres in which the mobility of water was particularly low.

So far, we have demonstrated some relationships between the water retention properties of fibres and the sequence of events and processes in drying web. Although the changes in tensile strength with drying have been discussed, little has been said about the relationship of water retention

properties to the level of strength development in the wet web or to the strength of the final sheet.

It is not possible, as might be suggested by a first look at Fig. 17, to relate the strength of the wet web to the tension in the residual water by assuming that the friction or cohesion of fibres is a simple function of the tension in the interfibre liquid films. The areas in contact and the mechanical interactions between the fibres depend additionally upon the morphology and deformability of the fibre, thus leading to a more complex picture.

It has been recognised for a long time, of course, that the strength of paper is correlated with the swelling[22, 28, 32-34] or water retention properties of the pulp fibres from which it is made and pulp evaluation is often identified with measurements based on the cellulose/water relationship.[35] At the same time, it must be recognised that the water retention properties of fibres can scarcely be identified or correlated with *all* the stock properties that contribute to sheet strength. It is a matter of observation, however, that many of those treatments that increase the water retention properties of fibres—beating, swelling, chemical modification—improve the strength of the sheet, whereas treatments that decrease water retention tend to impair it—drying, heating, dry cross-linking, hemicellulose removal. The explanation lies in the observation that an increase in water retention usually implies an increase in the surface area by fibrillation or an increase in the flexibility or conformability as a consequence of swelling and lowered cohesion in the fibre wall. These properties that are developed by mechanical or chemical means lead to increased bonding and strength at least up to the point at which the treatment reduces fibre strength by mechanical damage[27] or degradation of the cellulose by chemical attack. This general correlation of waterholding properties of a pulp with paper properties explains the successful use of a wide variety of pulp evaluation or control tests based on the cellulose/water relationship.

By far the greater number of the pulp evaluation tests (which are based on water retention or fibre swelling) are dynamic tests that are not related directly to the water retention at equilibrium with a specified force. Instead, they are empirical tests and variables such as the size of sample or the duration of the tests must be arbitrarily fixed. Such tests include freeness or slowness determinations, drainage rates, centrifuging,[33, 34] Imset evaluation,[36] suction[37] and drying rate methods.[38, 39] In many of these, the result is determined by the mobility of the water that is being removed or the tenacity with which it is held rather than by the equilibrium retention. In this respect, some of these tests are closer to papermaking practice than the equilibrium methods that have been described and they are of course much more rapidly performed.

The design of appropriate dynamic tests should be given consideration.

Since it is probably true that the amounts of water held by different mechanisms are held with varying tenacities and possess different mobilities, it is reasonable to suppose that dynamic, non-equilibrium tests could be designed to estimate or determine the amounts of water held by the various mechanisms. As an example, the measurement of drying rates has been applied to pulp and other cellulose fibres by previous workers. This method has been refined in one case[13] to the extent that five distinct consecutive slopes could be detected in drying rate curves and interpreted in terms of different retention mechanisms. Other applications have been less successful.

These and other dynamic non-equilibrium methods provide limited information because of arbitrarily fixed variables. If the choice of experimental conditions is appropriate, however, the amount of associated water that is measured by them can be significantly related to fibre or web properties of interest. The use of centrifuge techniques has been widespread and is attractive, because of speed and reproducibility and because the variables are easily changed. For example, Erfurt[40] has shown a good correlation between centrifugal water retention values and a change of rate of development of strength in a drying wet web. Thode & Ingmanson[28] have successfully correlated the centrifuge results with the hydrodynamic specific volume. Preston & Nimkar,[41] using textile fibres, have correlated centrifugal values with water retention measured on the porous plate. Samuelson[42] has increased the amount of information available from the centrifugal method by testing textile fibre samples at a series of rotor speeds. At the present time, however, most non-equilibrium methods are valuable only to the extent that the results are sensitive to the magnitude and direction of changes in stock make-up or treatment. Their value is as criteria of uniformity and as control methods rather than as methods producing data that are related in a quantitative or theoretical way to the physical behaviour of wet webs or paper.

Interest in the swelling and water retention properties of fibres is not restricted to the prediction of the dimensional stability, strength and other properties of paper. These fibre/water properties are important also in the various steps in the papermaking process. The swelling affects the flow and drainage properties of a fibre suspension by simple volume effects. The amount of water held by the fibres and the manner of its holding have their influence in the mechanical response of the web on the table, over the boxes and at the couch draw. The extent and mechanism of retention affects also the plastic and elastic resistance of the web to pressing, the incidence of crushing, the partition of water between felt and web or between web and cylinder in outgoing nips, the mechanism and rate of hot surface drying, the adhesion to drying cylinders, the efficiency of wet creping, the degree of shrinkage and the development of anisotropic strains and 'internal stresses' during drying.

Although the properties of water retention and the cellulose/water relationship generally are relevant to these aspects of papermaking, the practical use of the static or equilibrium measurements that we have been discussing remains to be demonstrated. Quantitative predictions of the behaviour of a stock on the papermachine may require water retention tests that more closely simulate machine conditions. The design and interpretation of such tests can be assisted by a knowledge of the mechanism and forces involved in water retention by fibres.

Comment

THE water retention isotherms described in this paper may be used to calculate a bulk modulus of the fibre wall material. The assumption is required that water removal will result in collapse of the cell wall without leaving voids or pores. Convincing evidence on this point is provided by Stone & Scallan (this symposium).

The modulus $M = V\, dp/dV$ may then be calculated by identifying the volume change with the loss of water for incremental changes in applied pressure. The modulus increases, of course, as the volume is reduced. Typical values for a never-dried pulp are—

$P,\ dyn/cm^2$	RVP	$M,\ dyn/cm^2$
2.7×10^6	0.998	2×10^7
1.45×10^8	0.90	1×10^9

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Discussion

Mr J. E. Luce—Robertson said that the static water retention methods have yet to have their practical use demonstrated. We have found in our laboratory that water retention at low hydrostatic tensions correlates well with interfibre bonding capability as measured by z-direction tensile tests on handsheets. This seems to hold for a wide variety of pulps. Since water retention measurements are quicker and easier than the transverse tensile tests, we have used them for screening experimental pulps for bonding ability.

Chairman—A point that passed unnoticed when Giertz gave his talk was his statement about cellulose not being the water-retaining part. We have to be careful there, because we know very well that pure cellulose does absorb large quantities of water. The question now is how shall we describe water retained by cellulose and distinguish it from the water we think to be associated with the hemicellulose. It is somewhat dangerous just to state that we have the cellulose microfibrils as entities that are not involved in the fibre/water interaction. We know from measurements of the broad band in the NMR curves that this band is affected by the removal of water and we consider this to be related to the interaction of water with the cellulose fibrils. We should not discuss the structure of the microfibrils, but rather comment about this question of the relationship between pure cellulose and water, because consolidation effects are not only a question of water and hemicellulose interaction.

Dr A. H. Nissan—When talking about cellulose and water, we should think of three celluloses. Cellulose is a general term. Ott, in his book on cellulose, has already explained that it has different meanings to the pure chemist than that understood in the commercial sense. With water, however, we must approach the molecule much more closely and regard it as a molecule of water. Cellulose has three different sites so far as water is concerned.

There is the portion of the cellulose inside the fibril, which recent studies seem to indicate are as near single crystals as you can make them. Therefore, to water, we have here a perfect crystal, well balanced; all the forces are satisfied and it has energy barriers that a water molecule cannot surmount, say, at room temperature. This being so, if the translation of energy of a molecule is

taken as $1\frac{1}{2}$ *RT*, it has no more than a few hundred cal/mole with which to penetrate into the crystal: this it cannot do. This is one site and the cellulose/ water relationship has one meaning there.

Another is the surface of the crystal, where the cellulose molecule is in a different state. One side of the molecule is satisfied, the other is not. The water molecule will therefore see and react with the surface in an entirely different manner from how it sees the molecule of cellulose inside the crystal. It will settle on and be tied tenaciously to the sites. It will have a special and peculiarly ordered state that is neither that of ice nor that of the cellulose crystal pattern: it is a special state of ordered water.

Then there is a third cellulose in the cellulose/water relationship—the totally disordered sites on which water will settle. Here, water is again tenaciously held, but it has no order.

We need therefore in such fundamental considerations to localise and focus our view very sharply on the portion of the cellulose molecule and its state: then we can say that cellulose does sometimes attract water, sometimes not.

Having said that, I would like to ask a question. Barkas made an extensive and somewhat difficult study of the thermodynamics of the cellulose/water relationship to provide a method whereby the amount of water to be expressed under pressure should be calculable, if we have the isotherms in the proper units. Have the studies reported by Van den Akker and others been related to Barkas' calculations to see whether in fact these pressures are calculable by Barkas' methods, which, so far as I know, have never been refuted?

Dr A. A. Robertson—I can give only a rather unsatisfactory answer. I reported that I had calculated bulk moduli on the assumption that water was being removed without leaving voids in the cellulose fibre—the cellulose was collapsing completely as Stone's evidence appears to show. I calculated moduli from isotherms and compared them with the compressibilities as measured by Van den Akker and Wink some years ago and, gratifyingly, the moduli were only 15–20 per cent different—quite the same order of magnitude and getting closer as one went to higher pressures. This is to be expected, in as much as Van den Akker's experiments related to the mechanical pressing of a pad of fibres: the higher the pressures, the less became the part played by the voids in the change of volume and the closer it approached a system in which the compressibility of cellulose itself was being measured. The agreement was fair, considering the difference in method.

Prof. Giertz—When presenting my paper, I was very careful not to give any accurate values for the specific water sorption capacity of cellulose and hemicellulose, respectively. We know that pulps rich in hemicellulose have a much

higher moisture absorption than have purified pulps such as high alpha viscose pulps or acetate grade pulps. We know, however, very little about the sorption of water when the fibre is dipped and wetted in water, both regarding quantity and mechanism, nor about the role that the hemicellulose plays in the subsequent swelling of the fibre.

Chairman—I agree entirely with Nissan's views on the cellulose/water relationship. Furthermore, the old picture of the cellulose microfibrils and the hemicellulose, developed 10–15 years ago, is still good and valid.

The only thing I would like to add is that, when a pulp fibre consolidates by water removal and pressing, I think the change is related to some molecular flow of hemicellulose. On the other hand, I do not think that the cellulose molecules become mobile in the process of consolidation; they are associated with the crystal network of the native cellulose microfibrils, where they are trapped and cannot move as separate chains. That is the main reason for the effects being quite different when the hemicellulose is removed from pulp fibres. Mobile segments of cellulose molecules may occur in regenerated cellulose.